TITLE OF THE INVENTION: PROCESS FOR THE PURIFICATION OF NF3

BACKGROUND OF THE INVENTION

[0001] There is currently a large and growing requirement for NF_3 in semiconductor manufacturing. One of the early processes for producing NF_3 involves the direct fluorination of ammonium ions by F_2 whereby gaseous F_2 is contacted with liquid (molten) ammonium acid fluoride (AAF) while gaseous NH_3 is separately contacted with the liquid AAF to generate ammonium ions. The early processes are operated to maintain a molar ratio of by-product HF to ammonia of 2.0 to 2.5 (melt ratio) in the reaction liquid and at temperatures above the melting point of ammonium bifluoride, NH_4HF_2, which is 127°C. Later processes for producing NF_3 effect the direct fluorination of ammonium bifluoride using increased HF/NH_3 melt ratios. These later processes resulted in superior NF_3 yields than when the lower melt ratio processes were used.

[0002] Purification of the NF_3 reaction product formed by the direct fluorination of ammonium bifluoride involves the removal of unreacted or unconverted F_2, as well as the byproducts HF, N_2, and trace levels of N_2F_2, and N_2O. Conventional practice in prior purification processes effects the removal of excess F_2 and co-product HF by aqueous KOH scrubbing followed by removal of trace levels of nitrogen oxides and water present in the stream using a solid molecular sieve adsorbent. Finally, the NF_3 is further purified using distillation.

[0003] The following patents and articles describe processes for production and purification of NF_3.

[0004] US 4,091,081 discloses a process for the production of NF_3 by the direct fluorination of ammonium bifluoride at temperatures above 260°F and below 400°F. An HF/NH_3 ratio of 2 to 2.5 is maintained. Purification is effected by passing the reaction product through a mist eliminator pad and then through an aqueous KOH scrubber. Residual HF and unreacted F_2 are removed in the scrubber. After scrubbing, the temperature of the stream is reduced to condense water and then the stream passed through molecular sieve driers for further purification.

[0005] US 4,156,598 describes a process for the production NF_3 by the direct fluorination of ammonium bifluoride. Purification of the gaseous reaction stream involves passing the gaseous reaction stream through a mist eliminator pad to remove entrained ammonium fluoride or bifluoride and then through a bath capable of forming a salt of HF and F_2, e.g., an aqueous KOH bath. Alternatively, sodium fluoride is used in place of KOH, but F_2 is not removed by this method. To extend the lifetime of the adsorber columns N_2F_2 is removed to a level below 0.03 volume percent before adsorption of N_2O and water.

[0006] US 4,543,242 describes a process for the production and purification of NF_3. NF_3 is purified by removing HF by condensation. Further purification of NF_3 is accomplished by wet scrubbing of NF_3 using aqueous KOH followed by treatment using a molecular sieve.

[0007] US 4,933,158 discloses a process for the purification of NF_3 produced by various methods, including the direct fluorination of ammonium bifluoride. Removal of N_2O, CO_2, and N_2F_2 from an NF_3 stream is accomplished by passing the stream through a thermally treated natural zeolite.

[0008] US 4,980,144 describes a process for purification of NF_3 containing hydrogen fluoride, and oxygen difluoride. In the described process, NF_3 is generated under conditions such that OF_2 is generated in amounts in excess of 700 ppm. Typically, the NF_3 is generated by a process referred to as molten salt electrolysis wherein a salt comprised of ammonium fluoride and HF are electrolyzed. In the NF_3 purification process, HF is removed first by contact with water or a caustic scrubber. Then, the OF_2 present in the stream is removed to a level below about 10 ppm by contacting the gas with an aqueous solution of sodium thiosulfate, hydrogen iodide, and sodium sulfide. The NF_3 stream is then passed through a zeolite molecular sieve to remove water.

[0009] US 5,637,285 discloses the production or NF_3 by the direct fluorination of ammonium bifluoride at a melt ratio of HF/NH_3 of at least 2.55.

BRIEF SUMMARY OF THE INVENTION

[0010] This invention describes an improvement in a process for purifying a nitrogen trifluoride (NF_3) stream containing unreacted F_2, HF and nitrogen oxides but substantially free of OF_2 wherein the F_2 and HF are removed first and then the nitrogen oxides are removed by adsorption. The improvement in the process resides in removing the F_2

from said NF_3 stream without generating oxygen difluoride, removing HF and then removing said nitrogen oxides by adsorption. Further purification can be effected as desired.

[0011] Significant advantages can be achieved by the process and these include:

an ability to increase the life of absorber beds employed in NF_3 purification;

an ability to selectively remove fluorine in a single step;

an ability to produce a valuable fluorine-containing product while effecting removal of unreacted fluorine; and,

an ability to reduce corrosion problems associated with the caustic scrubber, which often is responsible for a 2% loss in production due to downtime.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0012] The figure is a flow diagram for the production and purification of NF_3.

DETAILED DESCRIPTION OF THE INVENTION

[0013] This invention describes an improvement in a process for purifying nitrogen trifluoride (NF_3). In newly adopted processes for producing NF_3 in high yields, gaseous F_2, as the fluorine reactant, is contacted with a vigorously mixed ammonium acid fluoride complex wherein the ratio of equivalents of HF to NH_3 typically is such that a significant amount of fluorine, e.g., up to about 20%, typically 5 to 15% by volume can remain in the NF_3 product stream. The NF_3 stream also contains byproduct HF, and nitrogen oxides but is substantially free of oxygen difluoride (OF_2), i.e., typically, there is no OF_2 in these streams. Any NF_3 stream having residual fluorine and HF contained therein, but substantially free of OF_2 can be employed as a feedstream for the process.

[0014] It has been discovered that when the removal of residual HF and fluorine is effected using aqueous reactants such as aqueous potassium hydroxide, some of the fluorine reacts to produce small amounts, e.g., 50 to 100 ppm of oxygen difluoride. Furthermore, it has been found that this oxygen difluoride byproduct then is capable of reacting with the molecular sieve in the adsorber columns thereby shortening the service life of the adsorbent. Thus, processing NF_3 feedstocks containing a significant level of fluorine by conventional methods can cause problems associated with adsorber life.

[0015] A key to the improvement in the NF_3 purification process resides in removing unreacted F_2 from the NF_3 reaction product stream without generating oxygen difluoride and under such conditions so as not to remove a substantial amount of NF_3. This selective removal of F_2 without removing NF_3 is accomplished by contacting the NF_3 reaction stream containing unreacted fluorine with a metal or nonmetal component capable of converting the fluorine to a fluoride, preferably in solid form, or in a liquid or gaseous form having substantially lower vapor pressure than NF_3, for efficient removal. A metal or non-metal element, metal oxide, metal sulfide, metal nitride, metal phosphide, metal arsenide, metal carbide, metal carbonate, anhydrous metal hydroxide, metal silicide, metal germanide, metal boride and metal aluminide may be used for contacting the NF_3 reaction product under conditions for forming a metal and/or non-metal fluoride.

[0016] Hydrogen fluoride in the reaction product normally does not react with the metal or non-metal element component used for converting the fluorine to a fluoride, e.g., a metal such as tungsten or non-metal element such as carbon, to any substantial degree. HF, therefore, can be removed subsequent to F_2 removal. However, small amounts of HF will react and can be removed by the metal or non-metal element component. HF will react to a substantial degree with some of the other components such as metal oxides. If these components are used, then HF can be removed prior to removal of F_2. If removal of hydrogen fluoride is effected prior to removal of fluorine, such removal must be done under conditions such that oxygen difluoride is not formed. Removal of hydrogen fluoride, in that case, is accomplished in the absence of a water containing medium, e.g., by cryogenic condensation.

[0017] To facilitate an understanding of the invention, reference is made to the drawing. An NF_3 reaction product stream 2 containing typically 40 vol% NF_3, 35 vol% HF, 15 vol% F_2, 9 vol% N_2, 1 vol% N_2F_2, and trace N_2O, and substantially free of OF_2, obtained by the direct fluorination of ammonium bifluoride, is employed for illustration. The fluorine content typically ranges from 5 to 15%. In this embodiment of the process, the stream 2 is first passed to a condenser/separator 4 to remove HF. The HF is condensed in condenser/separator 4 and removed as a liquid. Condensation of HF can be effected at subatmospheric to super atmospheric pressure and temperatures below the boiling point. Typical condensation temperatures range from -78 to - 196 °C at atmospheric pressure. The condenser/separator is preferably operated under conditions sufficient to remove the maximum amount of HF with negligible NF_3 loss. Consequently,

the vapor feed stream from condenser/separator 4 typically will contain less than 10% HF and preferably less than 2% HF.

[0018] The effluent from the condenser/separator 4 is sent via line 6 to a fluorine reactor 8 to effect removal of unreacted F_2. The fluorine reactor is filled with a metal or non-metal component capable of converting the unreacted fluorine to a fluoride for effective removal. A metal, metal oxide, metal compound, nonmetal element, or anhydrous metal hydroxide that can react with gaseous F_2 to form a fluorine-containing product is suitable. Specific examples of metals and non-metal elements for forming metal and non-metal fluorides include silicon, tungsten, iron, zinc, zirconium, sulfur, and carbon; specific examples of metal oxides include aluminum oxide, zirconium oxide, iron oxide, magnesium oxide, strontium oxide, lanthanum oxide, and calcium oxide; specific examples of anhydrous hydroxides include anhydrous aluminum hydroxide, anhydrous calcium hydroxide, anhydrous strontium hydroxide, and anhydrous magnesium hydroxide; specific examples of carbonates include calcium carbonate and sodium carbonate, and, specific examples of carbides and sulfides include silicon carbide, iron sulfide, etc. For reasons of efficiency and economy metals and non-metals such as tungsten, silicon, sulfur and carbon are selected to provide a valuable metal fluoride product.

[0019] The fluorine reactor 8 can be in the form of a packed bed, a fluidized bed or trickle bed reactor or any combination of the above. Ambient temperatures and pressures may be used in the reactor due to the high reactivity of the metal component with the unreacted fluorine. The fluorine-containing product compound typically cannot be converted back to the metal or nonmetal element or metal oxide by simple means (e.g., pressure or temperature swing cycles), and is periodically removed in the product-fluoride form from the fluorine reactor 8 via line 10 and replaced with fresh starting material. The frequency of replacement is based on the reaction capacity for a particular starting material and concentration of F_2 (and possibly HF) in the feed. Volatile metal and non-metal fluorides can be removed by pressure reduction when the metals or non-metals are reacted to desired completion or removed as vapor along with the effluent NF_3 stream.

[0020] An effluent stream in line 12 from the fluorine reactor 8 generally consists of a mixture of NF_3 and N_2, and the fluoride-product if volatile, along with some nitrogen oxides. It generally will contain less than 15 ppm HF, less than 200 ppm F_2,

approximately 100 ppm N_2O and no detectable OF_2. In prior processes, the fluorine reacted with the aqueous hydroxide ion in the KOH caustic scrubber generating oxygen difluoride. But, by using a non-aqueous and anhydrous compound such as a metal or nonmetal to react with the fluorine, no or only a trace amount of oxygen difluoride is formed. In contrast to other NF_3 purification processes, an oxygen difluoride removal step is not required.

[0021] An alternate embodiment to the above process is to effect HF separation after selective removal of fluorine in fluorine reactor 8. The HF condenser/separator when placed subsequent to fluorine reactor 8 can use multiple methods for effecting removal which includes condensation, scrubbing in an aqueous alkaline solution, e.g., aqueous potassium or sodium hydroxide, or adsorption. Aqueous or alkaline systems for removing HF prior to removal of fluorine will result in the generation of oxygen difluoride and thereby defeat the purpose of selective removal of fluorine without generating oxygen difluoride.

[0022] The effluent gas from the fluorine reactor 8 is then sent via line 12 to an adsorber 14 to remove nitrogen oxides such as N_2O, as well as possibly water, and the like from the effluent stream. Conventional adsorbents such as silicate-based molecular sieves or zeolites, e.g., 3A, K-zeolite, chabazite, a mordenite or carbon-based molecular sieves are used in the adsorber to effect the removal of residual water, nitrogen oxides, and other byproducts. Finally, the effluent from the adsorber rich in NF_3 is sent via line 16 to a distillation column 18 for final purification. A purified NF_3 product is removed via line 20 as a middle cut, with N_2 removed via line 22 as an overhead stream. Residual metal fluoride which may have been carried through the process is removed via line 24.

[0023] In summary, operating the process under conditions for effecting the removal of fluorine from an NF_3 reaction product stream without forming byproduct oxygen difluoride extends the life of the adsorber beds and enhances the purification process.

[0024] The following example is illustrative of another embodiment.

[0025] An NF_3 reaction product stream 2 is generated in conventional manner by the fluorination of ammonium bifluoride at an NH_3/HF melt ratio of approximately 2.6. The reaction product stream typically contains 45% NF_3, 32% HF, 13% F_2, 9% N_2, 1% N_2F_2 and 500 ppm N_2O. HF is removed from this stream by passing it through a shell and tube condenser/separator 4 made of Monel® pipe with cooling liquid at –78°C from a dry ice/limonene bath circulating through the shell side at a pressure of 3 psig and flowing at

20 standard liters per minute (sLm). HF is liquefied and with even lower cooling liquid temperatures can be removed from the stream to a concentration <1.0%.

[0026] Fluorine is removed from the stream without forming OF_2 in a reactor constructed of Monel® pipe of 6-inch diameter equipped with a cooling jacket for circulating a cooling liquid. It is filled with 17 kg of tungsten metal powder (Type M63 from Osram Sylvania Co.) to give a bed height of 8-inches. This reactor is heated with a resistance heater to an initial temperature of 80°C. To effect removal, the stream, now containing 65% NF_3, 1% HF, 19%F_2, 13% N_2, 1.5% N_2F_2 and 700 ppm N_2O after removal of HF, is passed through the tungsten-filled reactor whereupon the F_2 reacts completely with the tungsten metal powder to generate tungsten hexafluoride (WF_6) gas at 16.7 g/min. The temperature of fluorine reactor 8 is maintained between 100 and 200°C by means of the cooling fluid circulating through the jacket. (The resistance heater is turned off because the reaction generates sufficient heat to sustain these temperatures.) The effluent stream in line 12 from the fluorine reactor 8 now contains 76% NF_3, <2ppm HF, <1ppm F_2, 15% N_2, <1ppm N_2F_2, 100ppm N_2O and 8% WF_6. From this it can be seen that nearly all the F_2 reacted with the tungsten without forming OF_2 and, also the HF and N_2F_2 is removed. N_2O is removed to a lower concentration.

[0027] Further purification of the NF_3 stream is done by passing the stream through an N_2O/H_2O adsorber 14 made of 3-inch diameter Monel® pipe packed with 3A molecular sieve and mordenite molecular sieve having a combined bed length of 24-inches. The effluent stream from adsorber 14 contains 76% NF_3, 16% N_2 and 8% WF_6. N_2O is reduced to <15 ppm. The effluent stream from the adsorber filled with a 3A molecular sieve and mordenite is sent to a distillation column 18 whereby the WF_6 is removed from the NF_3 as a higher boiling fraction from the bottom of the column via line 24 and the N_2 is removed from the NF_3 as a lower boiling fraction from the overhead via line 22. The purified NF_3 product is removed as a middle boiling fraction via line 20. The purity of the NF_3 processed in this manner is 99.996%. The WF_6 isolated from distillation column can be further purified to 99.9995% by distillation and can be marketed as a valuable co-product for use in semiconductor production.